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Second Quarterly Report
for
Sealing of Silver Oxide-Zinc Storage Cells
(23 September to 23 December 1967)

Contract No.: NAS 5-10409

Prepared by

Astropower Laboratory
Missile & Space Systems Division
Douglas Aircraft Company
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Newport Beach, California

for

Goddard Space Flight Center
Greenbelt, Maryland

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The objective of this program is to evaluate the use of miniature hybrid fuel cells in controlling pressure and thereby permitting operation of hermetically sealed silver oxide-zinc cells. The fuel cells perform this function by electrochemically consuming evolved hydrogen and oxygen. Two types of fuel cells are being used for this purpose. The first involves a silver oxide cathode in conjunction with a hydrogen-consuming anode. The second involves a cadmium anode in conjunction with an oxygen-consuming cathode. These fuel cells and their use in controlling pressure and in sealing batteries, including silver-zinc batteries, are proprietary with McDonnell Douglas Corporation, and are covered in one or more pending patent applications. The silver oxide-zinc cells under investigation are commercial 16-Ah high rate units.

Scope of the work consists of the following tasks:

- Task 1. Determine the gassing characteristics of the silver-zinc cells under four different operating regimes;
- Task 2. Design and test micro fuel cells to accommodate the gassing rates in these cells;
- Task 3. Evaluate composite micro fuel cell/silver-zinc cells in the sealed condition under the same regimes as indicated above;
- Task 4. Assemble and deliver 15 sealed silver oxide-zinc cell/micro fuel cell composites to NASA/Goddard for evaluation.

The major accomplishment during this report period was the successful completion of Tasks 1 and 2 above. Sufficient information was derived to begin Task 3. Most of the experimental effort was devoted to Task 1. This involved conducting extensive gassing studies on twenty-four commercial 16 Ah silver-zinc cells for two conditions of cycling and two conditions of open circuit stand. A final test series was carried out on factors which affect performance of micro fuel cells in order to complete Task 2. The most significant results and conclusions that can be derived from these investigations are given below.

1. Extremely low gassing rates were noted for each of eight silver-zinc cells when operated in series on a 24-hour cycle regime. This regime consisted of a modified constant potential charge for 23 hours to a 1.98 volt/cell cutoff and a 1-hour discharge across a fixed load at 30% depth. Throughout the course of this test, which lasted for 81 cycles or 1944 hours, the total amounts of gases evolved ranged from a low of 40 cc in one cell to a high of only 222 cc in another cell. In all cases most of this gas was oxygen with only trace amounts of hydrogen. Required capacity of an AgO micro fuel cell to consume all of the hydrogen evolved in the worst case has been calculated to be 50 mah for the entire

test. Required capacity of a Cd micro fuel cell to consume all of the oxygen in the worst case is slightly over 1 Ah for this period.

2. Moderate to low gassing rates were noted from all of eight identical silver-zinc cells when operated on a similar 90-minute regime with a 2.02-volt/cell cutoff. When this cutoff voltage was raised to 2.05 volts/cell, extremely high gassing rates (mostly oxygen) were noted from all cells. The regimes were nearly identical except for the upper voltage cutoff. These consisted of a modified constant potential charge for 1 hour to one of the above cutoff voltages and a 1/2-hour discharge at 15% depth. Operating time at the lower 2.02-volt cutoff was 1320 hours or a total of 880 cycles. During this period, the total amounts of gases evolved ranged from a low of 110 cc in one cell to a high of 268 cc in another cell. Oxygen was the major component in most cases, although some cells evolved appreciable quantities of hydrogen. Required capacity of an AgO micro fuel cell to consume all the hydrogen in the worst case was 0.21 Ah for this 880 hour-period. Required capacity of a Cd micro fuel cell to consume all the oxygen in the worst case was slightly less than 1 Ah. For the last 624 hours or 416 cycles at the 2.05 volt/cell cutoff the total gas evolved ranged from a low of 1138 cc in one cell to a high of 2638 cc in another cell. Appreciably larger quantities of hydrogen were evolved from the cells during this period, although the actual percentage of this gas was quite low due to the large quantities of oxygen also evolved. Required capacity of an AgO micro fuel cell to consume all the hydrogen during this period was 1.66 Ah in the worst case. Required capacity of a Cd micro fuel cell to consume all the oxygen during this period was 10.5 Ah.
3. Due to the exceptionally high capacity requirements of Cd micro fuel cells in the latter case, it became apparent that it would be necessary to operate this micro fuel cell in the secondary or regenerative mode. The results also indicate that it may also be desirable and perhaps necessary to operate the AgO micro fuel cells in this mode.
4. A final study on the effect of charge rate on performance of Cd and AgO micro fuel cells was carried out under Task 2. Results indicated a marked trend toward reduced capacity and discharge efficiency with increased charge rates in the range of 10 to 100 mA/cm².
5. Gassing and performance characteristics of the 16 Ah silver-zinc cells were determined under the conditions of special trickle charge and capacity discharge tests. These tests were performed on all the cells which had been on the continuous cycle regimes after 1320 hours of operation.
6. Simplified circuits have been designed for carrying out continuous recharge of the micro fuel cells. This involves

the use of a small auxiliary power supply to continuously apply a low trickle charge to the micro fuel cells while the sealed silver-zinc cells are on either charge, discharge or stand,

CONTENTS

INTRODUCTION	1
TECHNICAL DISCUSSION	2
Experimental Details	2
Description of Micro Fuel Cells	2
Description and Preliminary Treatment of Silver-Zinc Cells	2
Conduct of Gassing Studies	3
Measurement of Gassing	3
Operating Conditions for Stand Tests	3
Operating Conditions for Cells on 24-Hour Regime	3
Operating Conditions for Cells on 90-Minute Regime	3
Special Tests	4
Power Failure	4
EXPERIMENTAL RESULTS	4
Gassing and Operating Characteristics of Cells on the 24-Hour Regime	4
Gassing and Operating Characteristics of Cells on the 90-Minute Regime	7
Gassing Characteristics of Cells on Stand Tests	9
Special Tests	13
Micro Fuel Cell Requirements	14
Mode of Operating Micro Fuel Cells	18
Micro Fuel Cell Tests Under Task 2	19
Sealed Composite Assemblies	21
PROGRAM FOR THIRD QUARTER	25
REFERENCES	26

FIGURES

1	Typical Cycle Characteristics of Cells on 24-Hour Regime During Latter Stages (80 cycles)	6
2	Typical Gassing and Operating Characteristics of Ore All on the 90-minute Regime	11
3	Typical Cycle Characteristics of Cells On 90-Minute Regime During Latter Stages (1250 cycles)	13
4	Micro Fuel Cell Assembly	22
5	Silver-Zinc Cell and Micro Fuel Cell Charge and Discharge Circuits	23

TABLES

I	Gassing Characteristics of Eight Cells on 24 Hour Cycle Regime for 81 Cycles (1944 Hours)	5
II	Gassing Characteristics of Eight Cells on 90 Minute Cycle Regime for First 880 Cycles or 1320 Hours	8
III	Gassing Characteristics of Eight Cells on 90 Minute Cycle Regime for Last 416 Cycles or 624 Hours	10
IV	Micro Fuel Cell Requirements for Cells on 24 Hour Cycle Regime for 81 Cycles or 1944 Hours	15
V	Micro Fuel Cell Requirements for Cells on 90 Minute Cycle Regime for First 880 Cycles or 1320 Hours	16
VI	Micro Fuel Cell Requirements for Cells on 90 Minute Cycle Regime for Last 416 Cycles or 624 Hours	17
VII	Effect of Charge Rate on Capacity and Efficiency of CD Micro Fuel Cells	20
VIII	Effect of Charge Rate on Capacity and Efficiency of AgO Micro Fuel Cells	20

INTRODUCTION

The objective of this program is to evaluate the use of rechargeable micro fuel cells in controlling internal pressure of secondary silver oxide-zinc cells. This will permit operating these cells in the hermetically sealed condition under a wide range of operating conditions.

The miniature fuel cells perform this pressure control function by electrochemically consuming evolved gases (H_2 and O_2) from the silver-zinc cell. In practice, this is carried out by incorporating the miniature fuel cells directly into the gas head space of the silver-zinc cell or a small chamber which communicates with this head space. In this manner the miniature fuel cells are exposed to and consume the evolved gases.

The silver-zinc cells employed in this program were commercially available units from a leading manufacturer. They are high rate units with a nominal capacity of 16 Ah. Two types of micro fuel cells are involved in this program. One consumes hydrogen and the other consumes oxygen. The hydrogen-consuming cell is composed of a silver oxide cathode and a hydrogen gas anode. The oxygen-consuming cell is composed of a cadmium anode and an oxygen gas cathode.

The experimental effort was broken down into four tasks. The first task consisted of determining the gassing characteristics of the silver-zinc cells under two different cycle regimes and two conditions of open circuit stand. The second task consisted of designing and testing micro fuel cells to accommodate the gassing rates determined above. The third involves fabricating composite micro fuel cell-silver zinc cell assemblies and testing them in the sealed condition. The fourth and final task involves fabricating 15 additional composite assemblies and delivering them to NASA/Goddard for evaluation.

Major emphasis during this report period was placed on the gassing studies described above (Task 1). This involved measuring the gassing characteristics of 24 silver-zinc cells under different conditions for periods of nearly 2000 hours. Additional studies were also carried out on the micro fuel cells (Task 2). These were concerned with determining the effect of charge and discharge rates on capacity. Results in both of these areas are described here. Finally, the plans for Task 3 were formulated and laboratory preparations was begun.

TECHNICAL DISCUSSION

EXPERIMENTAL DETAILS

This section contains a brief description of the micro fuel cells involved and a complete description of the method and conditions for conducting gas-gassing studies on the silver-zinc cells.

Description of Micro Fuel Cells

A detailed description of the miniature fuel cell was given in the first quarterly report (Reference 1). Briefly, the silver oxide micro fuel cell is a cylindrical unit with overall diameter of 0.6 inch and length of 1 inch. The silver oxide cathode is a pellet type electrode. Electrolyte is potassium hydroxide solution. The separator is a proprietary inorganic type. The hydrogen anode is a commercial fuel cell type electrode from American Cyanamid (Type AB-40). Case material is lucite.

The cadmium micro fuel cell is a cylindrical unit with approximately the same overall dimensions as that of the silver oxide cell. The cadmium anode is a pellet type electrode. Electrolyte and separator are the same as above. The oxygen cathode is made from the same material as the hydrogen anode above.

Description and Preliminary Treatment of Silver-Zinc Cells

The silver-zinc cells were commercial 16 Ah high rate cells. Overall dimensions were approximately 2-1/4" x 4-13/16" x 13/16" (including terminals) and dry weight was 218 grams. Each cell was activated by 48 cc of electrolyte. The 24 cells were then divided into two groups of 12 each in series and carried through three formation cycles. This was done in accordance with the manufacturer's recommendations. Formation charge was carried out at constant current of 0.7 amp to a 2.05 volt per cell cutoff. Formation discharge was carried out at 5 amps to 1.0 volt per cell cutoff. The capacity of each of the cells was found to be at least 22 Ah as determined by individual discharges.

The cells were then divided into four groups for subsequent gassing studies. Four of these were set aside for a stand test at 0°C. These were numbered cells 1 through 4. Four more were set aside for a stand test at room temperature and were numbered cells 5 through 8. Eight were set aside for a 24-hour cycle regime and were numbered cells 9 through 16. The final eight were set aside for a 90-minute cycle regime and were numbered cells 17 through 24.

Conduct of Gassing Studies

Measurement of Gassing. — The displacement of water technique was employed for measuring gases evolved from the silver-zinc cells. This was carried out by connecting thin plastic tubing from the vent plug of each cell to an inverted cylinder filled with water. Gas composition was determined on a periodic basis by removing the graduate and analyzing a small sample in a gas chromatograph (Beckman Model GC 2-A). The analysis was entered in a logbook along with the volume accumulated. The graduate was then refilled for collecting more gases.

Operating Conditions for Stand Tests. — The stand tests at both room temperature and at 0°C were initiated with the cells in the fully charged state. Gas volume and open circuit voltage were measured periodically. There was very little if any gassing in any of these cells, so there was no need for analysis. The low temperature tests were carried out in a freezer set for 0°C.

Operating Conditions for Cells on 24-Hour Regime. — Conditions for this test were established after consultation with the technical monitor. It was decided that the eight cells were to be connected in series. Charge was to be carried out by a modified constant potential method with a voltage cutoff of 1.98 volts per cell. Initial charge current was to be set at 500 mA and time on charge was to be 23 hours. Discharge was to be carried across a fixed load selected so that the average current would be near 5 amps for one hour. These conditions were maintained throughout the test. The only minor discrepancy was that the average discharge current was slightly less than desired by about 10%. The power supply used was a Sorenson Model DCR 40-10A.

Operating Conditions for Cells on 90-Minute Regime. — Conditions for this test were also established after consultation with the technical monitor. The eight cells were to be run in series on a 90-minute regime in a similar manner to the above. Charge was to be carried out by the modified constant potential method with a voltage cutoff of 2.05 volts per cell. Initial charge current was to be 3.0 amps and time on charge was to be 1 hour. Discharge was to be carried out across a fixed load so that average current was near 5 amps for 1/2 hour. The above conditions were maintained during the latter stages of cycling, but not during the beginning. During the earlier period (the first 1320 hours), there was found to be a discrepancy between the intended and the actual end of charge cutoff voltage. The actual value was near 2.02 volts per cell, whereas the intended value was 2.05 volts per cell. The discrepancy was traced to two causes. First, it was found that the voltmeter used to set the power supply was slightly in error. Second, it was found that there was a small but significant IR drop in the lines from the power supply to the cell stack. These discrepancies were noted and compensated for by increasing output voltage of the power supply. During the last 624 hours of operation, the cells were run with a true 2.05 volt per cell cutoff. This adjustment was found to cause a marked increase in gassing rates.

Special Tests. — After 1320 hours, the continuous cycle tests of cells on both 24-hour and 90-minute regimes were interrupted temporarily for special tests. These consisted of a trickle charge test as well as a capacity discharge test. The trickle charge test was initiated at the end of a charge period. The cells were merely left on charge from this point for a period of two days. A detailed record was maintained of current variation, cell voltage and gassing rates during this period. The capacity discharge test was carried out at the end of this trickle charge. This involved a constant current discharge until the voltage of the last cell on each stack reached 1.0 volt. A detailed record was again maintained on cell voltages and gassing characteristics.

Power Failure. — The continuous cycling of cells on both regimes was also interrupted at an earlier time (after 670 hours) due to an overnight power failure in the laboratory. Due to the wiring arrangement of the timers and relays, this power failure caused all of the cells to become completely discharged. In order to recondition the cells they were subsequently carried through two more formation cycles. When it was established that all of the cells has regained their capacity and were functioning normally, the cycle tests were continued.

EXPERIMENTAL RESULTS

Gassing and Operating Characteristics of Cells on the 24-Hour Regime

In general, it may be stated that the cells on the 24-hour regime evolve extremely small quantities of gases. For example, the maximum amount of gas evolved from any one of the eight cells was only 222 cc for the complete cycle test (1944 hours or 81 cycles). In addition, it should be pointed out that there were extended periods in terms of a few weeks where some of these cells evolved almost no gases at all. In some cases, there were some signs of slow recombination as evidenced by a decrease in volume of gas within the cylinders.

A tabulation of the total amounts and composition of gases evolved from each of the eight cells for the complete cycle test is given in Table I. It is noted that the values range from a low of 40 cc in one cell to a high of 222 cc in another cell. Oxygen is the major constituent of the gases from all cells. In addition, it should be pointed out that most of this oxygen was evolved during the early stages of cycling after the initial formation cycles. The maximum amount of hydrogen evolved from any one cell was only 27 cc for the entire test.

The charge-discharge characteristics of the cells were quite uniform throughout the entire test. Typical cycle characteristics of both a single cell and the stack of eight cells are given in Figure 1. Initial charge current is noted to hold at 500 mA for about 1 hour, and then drops sharply to about 350 mA. For the next 22 hours, there is noted to be a gradual

TABLE I

GASSING CHARACTERISTICS OF EIGHT CELLS ON 24 HOUR
CYCLE REGIME FOR 81 CYCLES (1944 HOURS)

<u>Cell No.</u>	<u>Volume O₂ (cc)</u>	<u>Volume H₂ (cc)</u>	<u>Total Volume (cc)</u>
9	38	2	40
10	79	13	92
11	143	19	162
12	148	8	156
13	192	27	219
14	189	21	210
15	218	4	222
16	191	4	195

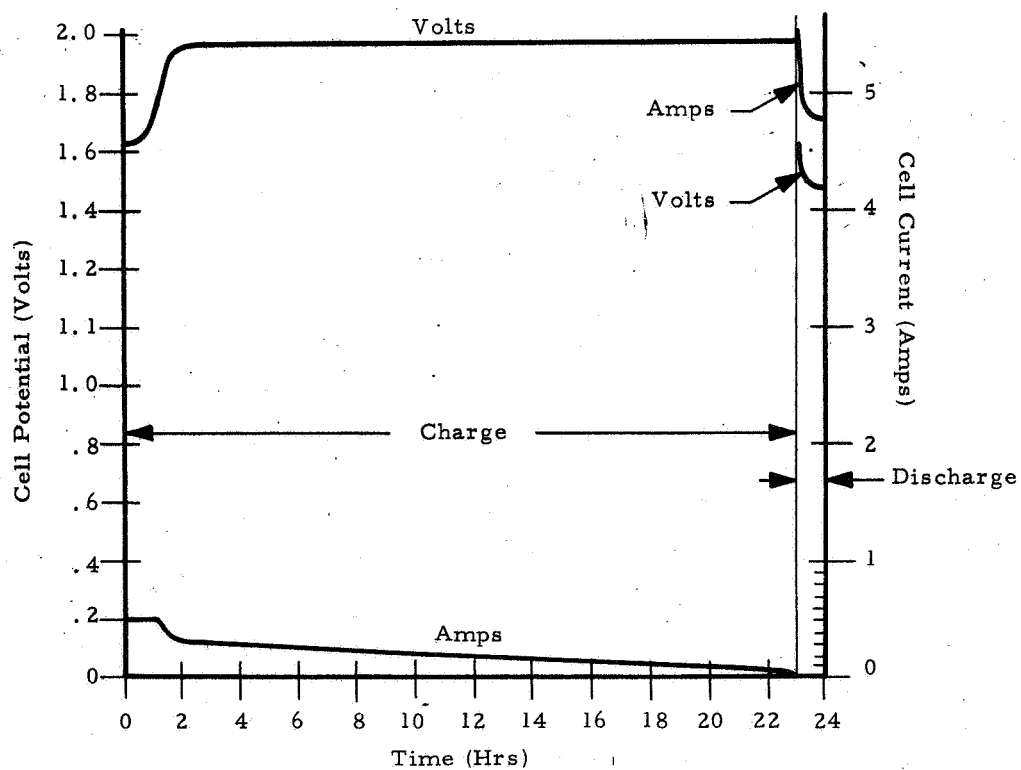
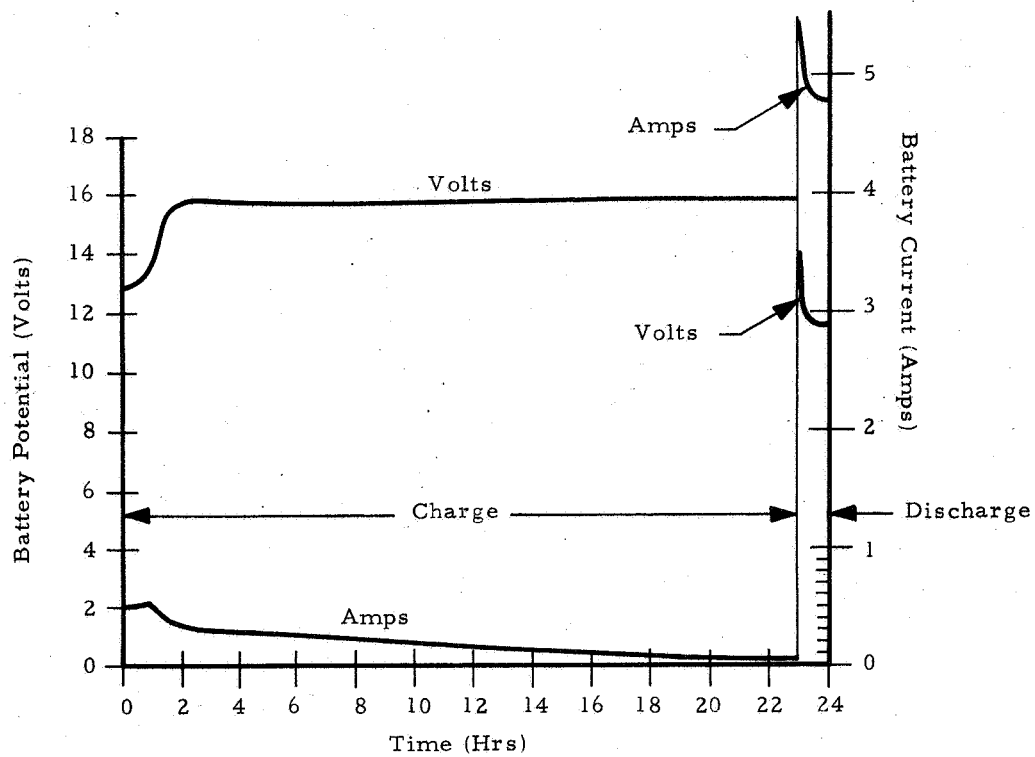


Figure 1. Typical Cycle Characteristics of Cells on 24-Hour Regime During Latter Stages (80 cycles).

decline to a level near 50 mA at the end of charge. This final end of charge current was noted to vary somewhat from day to day in the range of 10 mA to 80 mA. Discharge current is noted to drop quite rapidly during the first 5 minutes from 5.5 amps to 4.7 amps. Current remained constant at 4.7 amps throughout the balance of each 1-hour discharge.

End of discharge voltages were relatively uniform throughout the test. Except for the first few cycles, the end of discharge voltages were all in the range of 1.44 to 1.47 volts. End of charge voltages did vary somewhat from cell to cell and for individual cells during the course of the test. There were times when it appeared that there might be signs of unbalance as the spread in end of charge voltages ranged from 1.90 to 2.01. These differences became smaller, however, during the course of cycling. During the latter stages of cycling the spread in end of charge voltages was only 1.94 volts to 1.97 volts.

There was only one cell which exhibited rather unique characteristics. This was Cell #9. End of charge voltage on this cell was consistently lower than all the others until near the end of the test and was in the range of 1.90 to 1.94. It was also noted that there were no gases evolved from this cell at all until near the end of the test when end of charge voltage reached 1.96 volts. Aside from this one case, there are no other readily apparent correlations between electrical and gassing characteristics of the cells on this regime.

Gassing and Operating Characteristics of Cells on the 90-Minute Regime

As mentioned above, the marked differences in the gassing rates depended on the charging voltage cutoff level. During the first 880 cycles or 1320 hours, this cutoff voltage was near 2.02 volts per cell. During the last 416 cycles or 624 hours, this cutoff voltage was at a true 2.05 volts per cell. In view of these major differences, each interval will be examined separately.

Table II gives the total amount and composition of gases evolved from the cells on this regime for the first 880 cycles. Inspection of this data indicates that the gassing rates from the cells on this regime at a 2.02 volt cutoff are somewhat higher than the rates from the cells on the 24 hour regime which were at a 1.98 volt cutoff. However, the actual rates are quite small, especially in comparison with the rates found on these cells at a 2.05 volt cutoff. The maximum amount of gas evolved from any one cell at the 2.02 volt cutoff was 268 cc for the 880 cycles. The minimum amount was 105 cc for one cell during this period. Again it will be noted that in all cases the major portion of the gas was oxygen. Most of this oxygen was found to be evolved periodically during a one or two day interval when end of charge voltage on a given cell approached 2.10 volts. Very little, if any, oxygen was evolved at other times (this is discussed below). Hydrogen was found to be evolved quite slowly and uniformly in these cells at rates in the range of 1.0 to 2.0 cc H₂ per day.

TABLE II
GASSING CHARACTERISTICS OF EIGHT CELLS
ON 90 MINUTE CYCLE REGIME FOR FIRST
880 CYCLES OR 1320 HOURS

<u>Cell No.</u>	<u>Volume O₂ (cc)</u>	<u>Volume H₂ (cc)</u>	<u>Total Volume (cc)</u>
17	206	62	268
18	111	75	186
19	95	53	148
20	76	87	163
21	53	52	105
22	65	64	129
23	60	50	110
24	123	89	211

End of charge voltages during the interval were somewhat more erratic than those exhibited by the cells on the 24-hour regime. It was noted that there were intervals of one or two days during which the end of charge voltage of a given cell would progressively increase and then decrease each cycle from a level below 2.00 volts to a maximum near 2.10 volts, and then below 2.00 volts once again. Simultaneously there was noted to be a marked increase and then decrease in oxygen evolution. There was no apparent pattern to the occurrence of this phenomenon, but it did occur in all of the cells at least once during this interval. The amount of oxygen evolved from a cell during these periods was about 100 cc O₂ per day. End of discharge voltages were quite uniform for all the cells during this period and were in the range of 1.44 to 1.48 volts.

Gassing data for these cells at the 2.05-volt cutoff for the remaining 416 cycles are given in Table III. Inspection of this data indicates a marked increase in overall gassing rate of all cells. The maximum additional gas evolved from any one cell during the period was 2057 cc. As before, the major portion of this gas was found to be oxygen. This gas was evolved at the end of a charge cycle on cells with voltages in excess of 2.05 volts. Figure 2 gives the gassing characteristic of such a cell for a typical cycle. Here it is noted that the first signs of gassing occur after approximately 48 minutes of the 60-minute charge period. Gassing rate and also cell voltage are noted to increase quite rapidly at this point and current is noted to taper to lower levels. This trend continues until the end of the charge period when gassing rate falls sharply. The total amount of gas evolved during this cycle was 5.7 cc for this case. Other cells have been noted to evolve larger quantities during these periods with a maximum of approximately 11 cc of gas per cycle. Performance characteristics of both the stack of eight cells and one single cell for a typical cycle during the latter stages are given in Figure 3.

Although the average gassing rates in all the cells were much higher during this period, it should be pointed out that the rates were not always constant. There were times when a given cell would exhibit very high rates and end of charge voltages for several cycles and then exhibit relatively low rates and end of charge voltage for subsequent cycles. No definite pattern to this phenomenon was noted, however, it did occur in each cell at least once during the final 416 cycles.

Although the gas analyses performed during this period indicated relatively small percentages of hydrogen, the actual amounts of this gas were not necessarily negligible. This is because the quantities of gas were very large during the period. One cell, for example, evolved a total of 696 cc H₂ during this period. This amount definitely warrants a hydrogen-consuming micro fuel cell, as will be discussed below.

Gassing Characteristics of Cells on Stand Tests

No measurable amounts of gas were evolved from any of the four cells on stand at 0°C for the entire test, which lasted for 1944 hours.

TABLE III
GASSING CHARACTERISTICS OF EIGHT CELLS ON
90 MINUTE CYCLE REGIME FOR LAST
416 CYCLES OR 624 HOURS

<u>Cell No.</u>	<u>Volume O₂ (cc)</u>	<u>Volume H₂ (cc)</u>	<u>Total Volume (cc)</u>
17	2057	533	2590
18	1339	93	1432
19	2197	476	2673
20	1392	106	1498
21	1127	12	1139
22	1823	237	2060
23	1942	696	2638
24	1247	241	1488

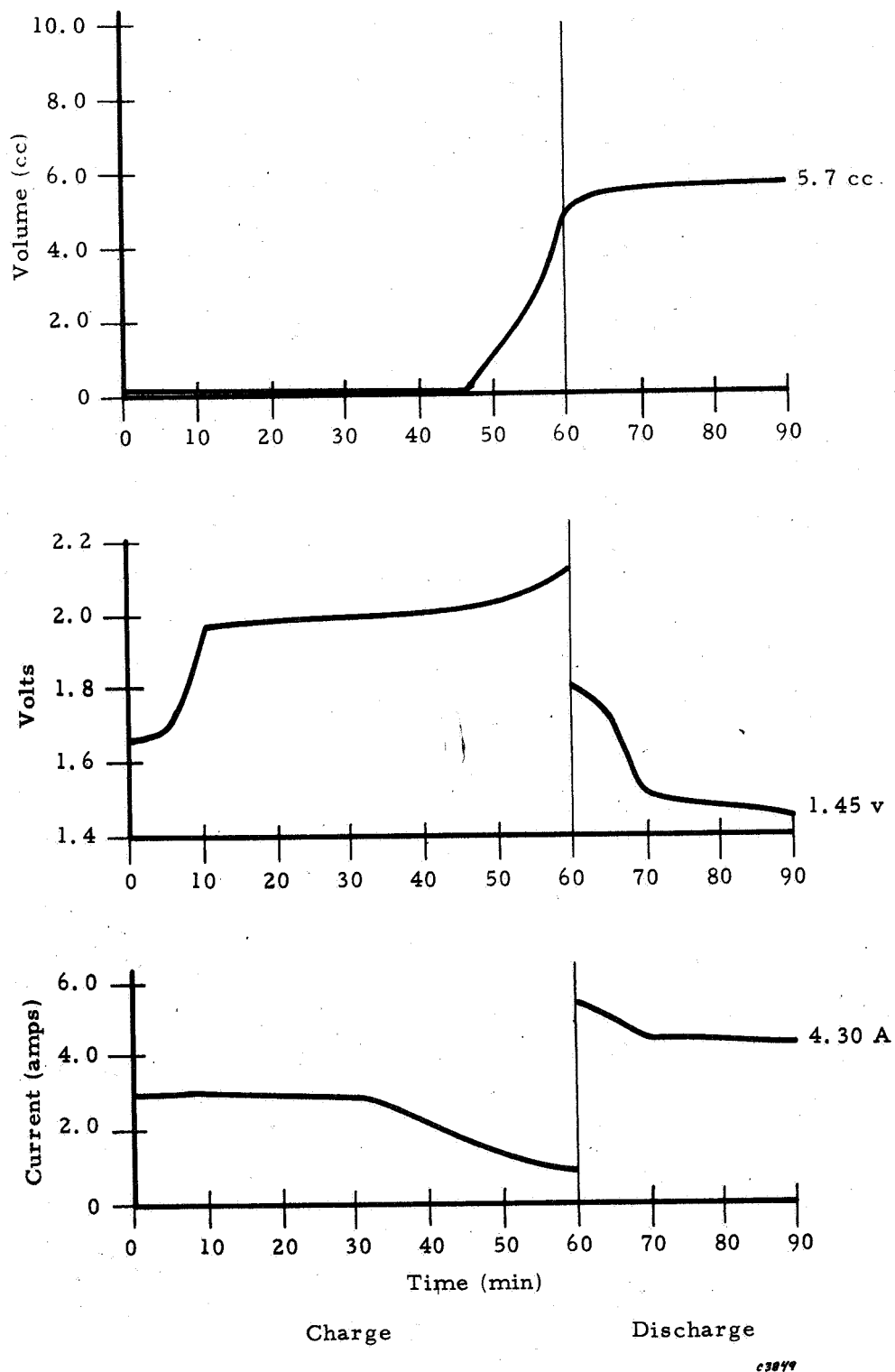


Figure 2. Typical Gassing and Operating Characteristics of Ore All on the 90-minute Regime.

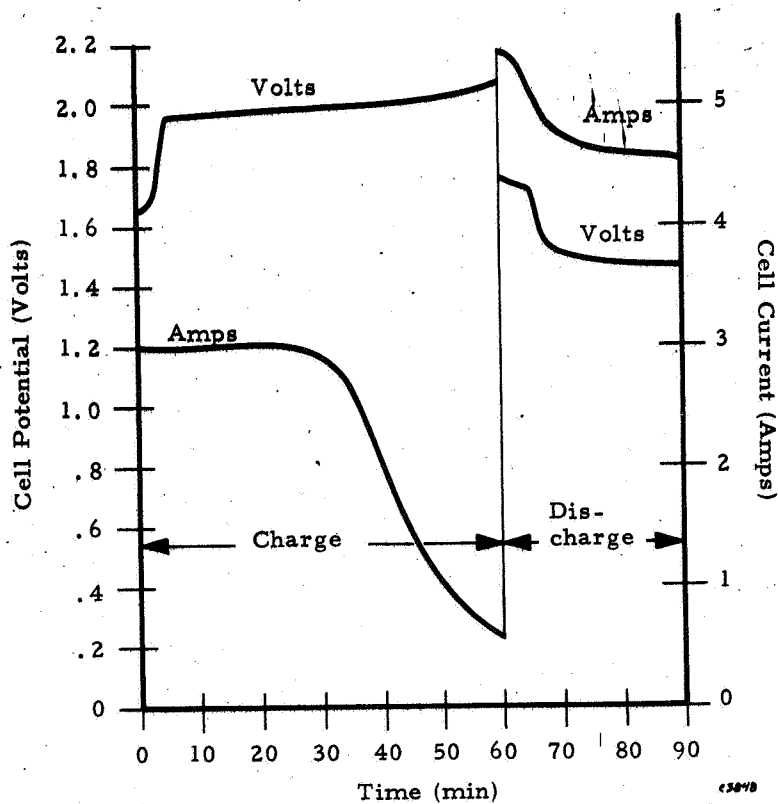
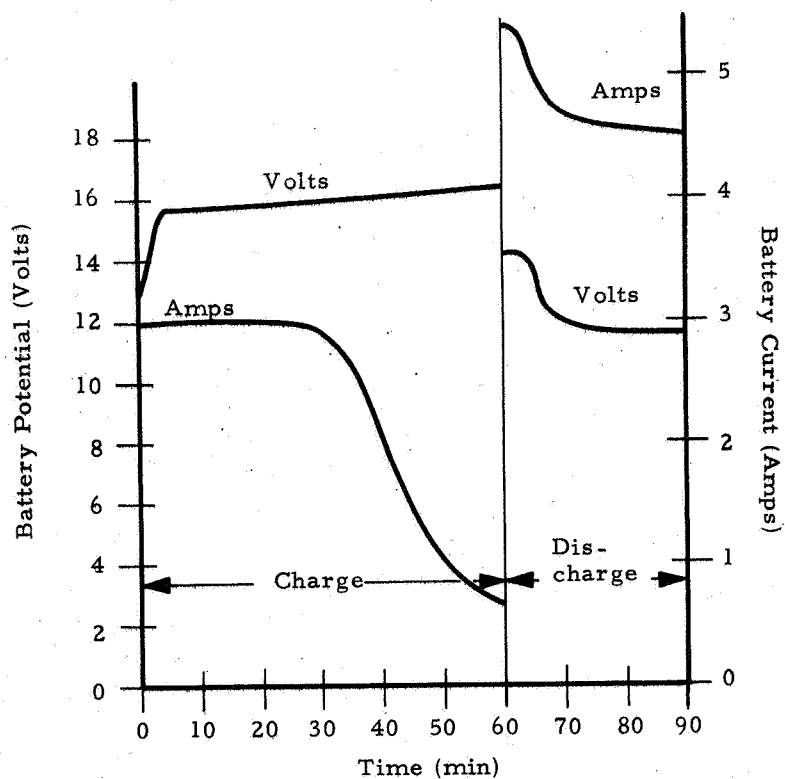


Figure 3. Typical Cycle Characteristics of Cells On 90-Minute Regime During Latter Stages (1250 cycles).

Very low hydrogen evolution rates (approximately 1cc/day) were noted from two of the four cells on room temperature stand for the first few weeks. Thereafter, the gassing rates from these cells was reduced to almost zero. No measurable amounts of gases were evolved from the other two cells on room temperature stand for the entire 1944 hours.

Special Tests

As mentioned above the continuous cycle tests on cells on both regimes were interrupted for several days in order to conduct special trickle charge and capacity tests.

The trickle charge on the cells that had been on the 24-hour regime was initiated at the end of a charge cycle. Total operating time in this mode was 48 hours. Charge current continued to taper for the first 10 hours from a level near 30 ma to a level near 5 ma. During the last 38 hours an almost steady state current of 4 ma was maintained. End of charge voltages were 1.97 volts for all cells except one which was 1.92 volts. The maximum amount of gas evolved from any one cell was 44 cc and there were two cells that did not evolve any gas during this period. The maximum gassing rate from any one cell was 0.8 cc/hr at the end of the test.

The capacity test on these cells was carried out at the end of the trickle charge test. Discharge current was 5.2 amps at the beginning and 0.5 amps at the end. The first cell reached 1.0 volt after 4.63 hrs at which point its output was 21.0 amp-hrs. The last or eighth cell reached 1.0 volt approximately 1.5 hours later. During this final 1.5-hr period there were three cells that exhibited cell reversal to the extent of -0.1 volt. Only one of these cells evolved measureable quantities of gas (20 cc).

In addition, the trickle charge test on the cells that had been on the 90-minute regime was initiated at the end of a charge cycle. Total operating time was 45 hrs. Charge current continued to taper for the first 24 hours from a level near 80 ma to a level near 40 ma. This final current was maintained for the final 21 hrs. End of charge voltages were 2.02 to 2.03 volts for all cells. The maximum amount of gas evolved from any one cell was 541 cc during this period. All cells were gassing at relatively constant rates at the end of the test with rates ranging from 8.2 to 13.6 cc/hr. The capacity test on these cells was carried out at the end of the trickle charge test. Initial discharge current was 5.2 amps and final current was 1.3 amps. The first cell reached 1.0 volt after 4.50 hours at which point it had delivered 19.1 amp-hrs. The last or eighth cell reached 1.0 volt after 5.55 hrs. During this latter interval there was only one cell which exhibited reversal to the extent of -0.08 volts. Two cells evolved significant quantities of gas during this latter interval to the extent of 100 to 120 cc. All other cells exhibited little or no gassing throughout the capacity test.

Micro Fuel Cell Requirements

The required size and capacity of micro fuel cells for the silver-zinc cells can be readily determined from the gassing data presented above. Capacity is calculated on the basis of the volume of gas evolved from a given cell. In the case of hydrogen, this involves multiplication of the total volume of this gas from a given cell by the known conversion factor of 1.0 Ah/420 cc H₂. In the case of oxygen, this factor is 1.0 Ah/210 cc O₂. The resulting values give the required capacities of silver oxide and cadmium micro fuel cells for consumption of these gases. The actual amounts of these electrode materials are then calculated on the basis of their known electrochemical equivalents and experimentally determined efficiencies which are near 90% for AgO and near 50% for Cd. The required area of the micro fuel cell electrodes depends on their operating current density, which can range to 50 mA/cm², and the required current, which is a direct function of the gassing rate. As has been pointed out above, the gassing rates have been found to vary from cell to cell and for a given cell from cycle to cycle. Since the current requirements will vary in a similar manner, it is readily apparent that there is no rigorous method for calculating the required area of the micro fuel cell electrodes. One conservative approach to this problem would be to design for the maximum gassing rate and corresponding maximum current. This, however, could result in an excessively large fuel cell, especially in the case of a cadmium cell, to consume the oxygen in cells on the 90-minute regime with a 2.05 volt cutoff. A more practical solution would be to select an intermediate size micro fuel cell area which could accomodate all of the gas at a moderate rate over a long period and not necessarily as rapidly as the gas is generated. This would result in some internal pressure rise during periods of rapid gassing and gradual decline in pressure thereafter. The operating current in this case would be within the capabilities of a moderate or small size fuel cell. The value of this current is readily calculated by dividing the total required capacity for a long interval by the operating time. This has been termed the "average required current" in the discussion which follows.

Results of calculations performed in this manner are given in Table IV for cells on the 24-hour regime and in Tables V and VI for cells on the 90-minute regime. Inspection of Table IV indicates that the total capacity requirements for consuming hydrogen are very small for cells on the 24-hour regime. Overall values range from a low of 5 mah to a high of 50 mah for the entire 81 days of operation. This indicates that an extremely low capacity AgO cell would be required, if at all. It may very well be that a hydrogen consuming cell may not be required at all as this small amount of hydrogen could possibly be consumed by slow chemical recombination with the cathode of the silver-zinc cell. Average current from an AgO cell, if it were employed, would be in the micro amp range with a maximum of only 34 μ a. Requirements for oxygen consumption in the cells on the 24-hour regime are somewhat more than the requirements for hydrogen. Required capacities of cadmium micro fuel cells would range from a low of 181 mah to a high of 1030 mah, or nominally 1.0 Ah for the 81 days. The corresponding average currents for these fuel cells would range from .10 mA to 0.54 mA for this period. Again, it may be pointed out that these calculated

TABLE IV

MICRO FUEL CELL REQUIREMENTS FOR CELLS ON
24 HOUR CYCLE REGIME FOR 81 CYCLES
OR 1944 HOURS

<u>Cell No.</u>	<u>Required Capacity of Cd Cell (mah)</u>	<u>Required Average Current from Cd Cell (ma)</u>	<u>Required Capacity of AgO Cell (mah)</u>	<u>Required Average Current from AgO Cell (ma)</u>
9	181	.09	5	3
10	375	.19	31	16
11	770	.40	45	23
12	740	.38	19	10
13	910	.47	64	33
14	900	.46	50	25
15	1030	.53	10	5
16	905	.46	10	5

TABLE V

MICRO FUEL CELL REQUIREMENTS FOR CELLS ON
90 MINUTE CYCLE REGIME FOR FIRST 880
CYCLES OR 1320 HOURS

<u>Cell No.</u>	<u>Required Capacity of CD Cell (mah)</u>	<u>Required Average Current from CD Cell (ma)</u>	<u>Required Capacity of AgO Cell (mah)</u>	<u>Required Average Current from AgO Cell (ma)</u>
9	181	.09	5	3
10	375	.19	31	16
11	770	.40	45	23
12	740	.38	19	10
13	910	.47	64	33
14	900	.46	50	25
15	1030	.53	10	5
16	905	.46	10	5

TABLE VI

MICRO FUEL CELL REQUIREMENTS FOR CELLS ON
90 MINUTE CYCLE REGIME FOR LAST
416 CYCLES OR 624 HOURS

<u>Cell No.</u>	<u>Required Capacity of CD Cell (A. H.)</u>	<u>Required Average Current from CD Cell (ma)</u>	<u>Required Capacity of AgO Cell (mah)</u>	<u>Required Average Current from AgO Cell (ma)</u>
17	9.80	15.7	1270	2.0
18	6.38	10.4	220	0.4
19	10.46	16.5	1130	1.8
20	6.64	10.6	250	0.4
21	5.42	8.7	30	0.05
22	8.73	14.0	570	0.9
23	9.25	14.8	1660	2.7
24	5.93	9.5	570	0.9

cadmium micro fuel cell requirements may be somewhat in excess of the actual requirements for some of the oxygen would undoubtedly be consumed by chemical recombination with the zinc anode.

Micro fuel cell requirements for cells on the 90-minute regime are somewhat different from those for cells on the 24-hour regime. With the 2.02 volt cutoff the requirements are somewhat larger and with a 2.05 volt cutoff the requirements are exceptionally large. Let us first examine the requirements for the 1320 hours at the 2.02 volt cutoff. Table V indicates that the required capacities of AgO micro fuel cells would range from 0.13 to 0.21 Ah. The corresponding average current from the AgO cells would range from 0.10 mA to 0.16 mA for this period. Required capacities of cadmium micro fuel cells during this period are noted to range from 0.25 to 0.98 Ah. The corresponding average currents from cadmium micro fuel cells would range from 0.19 mA to 0.45 mA.

For the last 624 hours at the 2.05 volt cutoff, the micro fuel cell requirements are noted to be exceptionally high, especially for oxygen. A summary of these requirements is given in Table VI. Required capacities of AgO micro fuel cells for hydrogen are noted to range from 0.03 to 1.66 Ah. The corresponding average current from AgO cells ranges from 0.05 mA to 2.77 mA. Required capacities for cadmium micro fuel cells on the other hand range from 5.42 Ah to 10.46 Ah. These values are excessively high for primary type micro fuel cells, and necessitate the use of a rechargeable type micro fuel cell. This will be discussed in the next section. The required average current from cadmium micro fuel cells during this period are in the range of 9.01 mA to 17.4 mA. These values are relatively high but not excessively so for the size of micro fuel cells employed here. This will also be discussed in the next section.

There are no micro fuel cell requirements for the silver-zinc cells on both room temperature stand or 0°C stand. Even if one neglects the chemical recombination factors, the maximum pressure that could result from the small amount of gases could be readily contained by the battery case.

Mode of Operating Micro Fuel Cells

There are several modes that can be employed in operating the micro fuel cells. Two general methods are the primary mode and secondary or rechargeable mode. The primary mode is applicable to the condition where gassing rates are very low. In this case, the micro fuel cells have sufficient capacity to consume all the gases over extended operating periods or even for the life of the battery. The micro fuel cells are merely inserted in the battery and placed on continuous discharge across a fixed load. No maintenance of the micro fuel cell is required for this condition.

The secondary mode is for the condition where gassing rates are very high. Required capacities are so large in this case that the required size of the micro fuel cells would be impractical. Operation is therefore carried out with a small micro fuel cell that is regenerated or recharged periodically

or continuously while in use. This charge is not carried out in the conventional manner (from fuel cell anode to cathode), but rather from the "solid" micro fuel cell electrode to one of the electrodes of the silver-zinc cell. Electrolyte path in this case is provided by a wick bridge. This method, which has been described previously, avoids generation of gas by the micro fuel cell. Several schedules for charging the micro fuel cells can be employed. One could consist of a slow and continuous trickle charge. A second could consist of a periodic charge every few days or whenever needed. A third could consist of routine short term charges as for example during each hour while the silver-zinc cells are being charged on a 90-minute regime.

In addition to the possible variations in charge schedules there are also variations in the methods for making external electrical connections to a group of micro fuel cells in a battery of silver-zinc cells. First of all, one could employ either a series or parallel charge circuit for charging both the silver oxide and cadmium micro fuel cells. Secondly, one could employ a charge of a given micro fuel cell electrode against either the silver-zinc cell anode or cathode. For example, one could charge the silver oxide micro fuel cell electrode against either the silver oxide cathode or zinc anode of the silver-zinc cell. Also, one could charge the cadmium micro fuel cell electrode against either of the two silver-zinc cell electrodes.

All of the above methods for operating the micro fuel cells were considered for the third phase of this program where the sealed tests will be carried out. After consultation with the technical monitor concerning the merits and limitations of the various methods, it was decided to proceed under conditions discussed in a subsequent section.

Micro Fuel Cell Tests Under Task 2

Two series of tests were carried out on Cd and AgO micro fuel cells to determine the effect of charge current density on capacity and efficiency. Results of these tests are given in Table VII for Cd cells run on oxygen and Table VIII for AgO cells run on hydrogen. Electrode areas in both cases were 1.0 cm^2 so that the indicated currents in mA are actually current densities, i.e., mA/cm^2 . The Cd electrodes employed here weighed 5.7 grams each and had a theoretical capacity of 2.5 Ah. The AgO electrodes weighed 3.2 gms and had a theoretical capacity of 1.4 Ah.

Results on both series of tests indicated a definite trend toward reduced capacity and efficiency with increased charge current. Output and efficiency of the Cd cells, for example, are noted to be reduced by almost 50% as charge current is increased from 10 to $100 \text{ mA}/\text{cm}^2$. Similarly, the output and efficiency of AgO cells are noted to be appreciably reduced as charge current is varied over the same range. The cause for these trends is attributed to inefficiencies in the charging process at high current densities. At these high rates and corresponding high voltages, a significant portion of the input current results in gas evolution at the micro fuel cell electrodes rather than the desired electrochemical reaction. This was substantiated in high rate charge of the Cd cells where the effluent gas was found to contain appreciable amounts of hydrogen.

TABLE VII
EFFECT OF CHARGE RATE ON CAPACITY AND
EFFICIENCY OF CD MICRO FUEL CELLS

<u>Charge Current (ma)</u>	<u>Discharge Current (ma)</u>	<u>Output (mah)</u>	<u>Efficiency (%)</u>
10	5	1250	50
20	5	1083	43
50	5	919	37
100	5	668	27

TABLE VIII
EFFECT OF CHARGE RATE ON CAPACITY AND
EFFICIENCY OF AgO MICRO FUEL CELLS

<u>Charge Current (ma)</u>	<u>Discharge Current (ma)</u>	<u>Output (mah)</u>	<u>Efficiency (%)</u>
10	5	1020	74
20	5	900	65
50	5	635	46
100	5	600	43

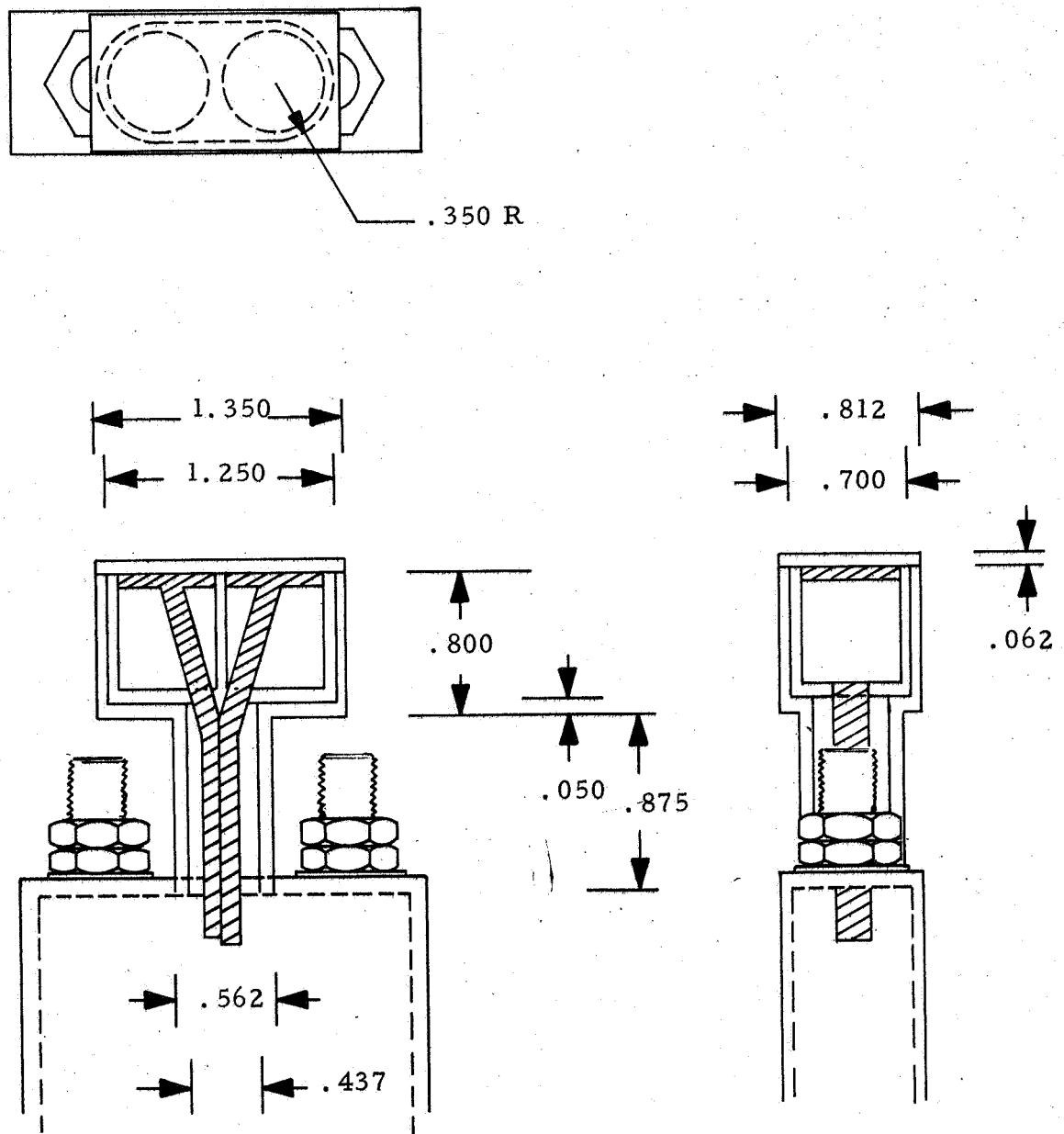
Sealed Composite Assemblies

After having successfully completed the battery gassing studies (Task 1) and the micro fuel cell design studies (Task 2), it was now possible to begin the third phase of this program (Task 3). This consists primarily of conducting cycle tests on sealed composite assemblies, the designs for which are based on results obtained in the two preceding phases. Several preliminary tasks are in process for this phase including the design and fabrication of the micro fuel cells and their adapters, the design of electrical circuits, and conducting formation cycles on new 16 Ah silver-zinc cells. These components will subsequently be assembled and placed into operation.

Figure 4 is a schematic diagram of one such composite assembly. The two fuel cells (AgO and Cd) are shown to be contained within a rectangular type adapter which in turn fits into the top of the silver-zinc cell. The fuel cells are attached to and suspended from the cover of this adapter with their gas consuming electrodes at the bottom. A wick is incorporated in each micro fuel cell and extends from the solid micro fuel cell electrode to the electrolyte of the silver-zinc cell. Electrical leads from the micro fuel cells are passed through the cover of the adapter for external electrical contact. In this manner, the complete sealing of the silver-zinc cell is achieved. The mode for operating the micro fuel cells has been finalized. It should be pointed out, however, that both types can readily be operated in either the primary or secondary mode.

The circuit for operating the micro fuel cells in the primary mode merely involves connecting the external terminals of each micro fuel cells in series with a suitable resistor and milliammeter or milliammeter recorder. The circuit to be employed for operating the micro fuel cells in the secondary mode is described as follows. For the sake of this discussion, we will examine the circuit for the Cd micro fuel cells. The same principles would, of course, apply to the AgO micro fuel cells. However, the results of Tasks 1 and 2 indicate that it would not be necessary to recharge the silver oxide micro fuel cells until possibly the end of this phase. Provision has been made for doing this when necessary; the integrated current-time reading of the silver oxide micro fuel cells would signal this requirement.

The method of charging the Cd micro fuel cell consists of a continuous trickle charge carried out in parallel. Figure 5 is a schematic circuit diagram for this method. A battery of eight silver-zinc cells, each containing a micro fuel cell, is connected in series. These eight Ag-Zn cells are cycled (charged and discharged) in accordance with a specified cycle regime. A constant current/constant voltage DC power supply is employed to charge the eight Ag-Zn cells at a constant current to a pre-set upper voltage limit. When the charge voltage of all eight cells reaches the pre-set voltage (eight times the single cell voltage), the charge current is then reduced to a value which maintains this end charge voltage for the remaining charge period. The cells are then switched to a fixed resistive load (rheostat) for discharge at a determined current rate. A cycle regime timer times out the charge and discharge periods and alternately switches the series connected Ag-Zn cells from the charging power supply to the load bank. A separate relay



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Figure 4. Micro Fuel Cell Assembly

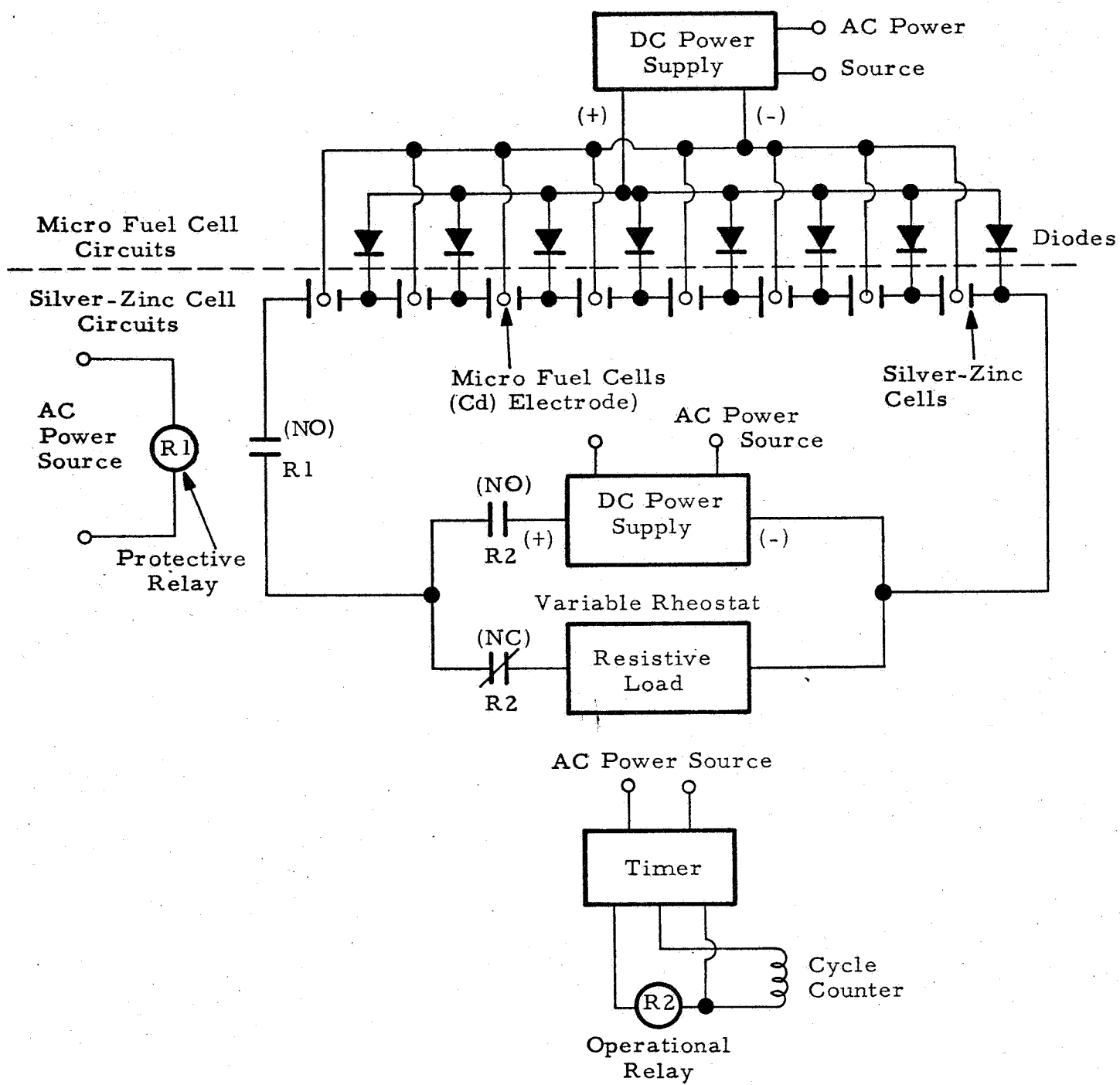


Figure 5. Silver-Zinc Cell and Micro Fuel Cell Charge and Discharge Circuits.

operated by the AC power source is used to open the charge-discharge circuit should an AC power failure occur, thereby protecting the Ag-Zn cells from accidental discharge. An electrically operated counter will accumulate the number of charge-discharge cycles obtained.

As indicated in the schematic diagram, Figure 5, the eight cadmium micro fuel cells are continually charged in parallel by means of a separate constant current/constant voltage DC power supply. The positive terminal of this power supply is connected to each negative (zinc) electrode of each of the eight silver-zinc cells by a parallel connection. Each parallel connection contains a Motorola 1N4001 protective diode (rated at 50 volts, 1 ampere) to prevent shorting the Ag-Zn cells through the micro fuel cell circuit. The negative terminal of this power supply is connected to each cadmium electrode of each Cd micro fuel cell by a parallel connection. The power supply continually charges each micro fuel cell Cd electrode at a current which will depend upon the gassing rate of the Ag-Zn cell. When the charge voltage of each micro fuel cell reaches the pre-set upper voltage limit, indicating a full state of charge, the charge current will taper off to a low value such that the upper voltage limit will not be exceeded. This method will avoid overcharging the micro fuel cell cadmium electrodes and subsequent evolution of hydrogen. Each micro fuel cell will therefore be maintained as close as possible to a full state of charge while at the same time it consumes the oxygen evolved from the Ag-Zn cell.

The current output of each micro fuel cell will be monitored in the same manner as in the primary mode described previously. Current input to each micro fuel cell can be monitored by incorporating a milliammeter or current recorder in each of the parallel micro fuel cell circuits.

Instrumentation, which is not shown in the Figure 5 schematic diagram, will be provided for continuously monitoring all silver-zinc cells on each cycle regime. Rustrak DC voltage recorders and pressure recorders will be used to record each Ag-Zn cell voltage and internal pressure throughout each charge and discharge. Also, Weston 911 DC ammeters will indicate the charge and discharge current of the Ag-Zn cells, as well as current output of both AgO and Cd micro fuel cells.

PROGRAM FOR THIRD QUARTER

Experimental effort during this period will be devoted exclusively to testing composite micro fuel cell-silver zinc cell assemblies. Sixteen such composite assemblies have been fabricated and are about to be placed under test. Eight of these will be cycled on the 24-hour regime and eight more will be cycled on the 90-minute regime. Eight more assemblies will be fabricated for the 0°C and 25°C stand tests if thought advisable by the contract monitor.

The cycle tests will be carried out in accordance with the procedures outline in the previous section. Complete records will be maintained on performance of micro fuel cells and silver-zinc cells throughout the test.

REFERENCES

1. "Sealing of Silver Oxide-Zinc Storage Cells," First Quarterly Report, Contract No. NAS 5-10409, Douglas Aircraft Company Report DAC-59860-Q1, September 1967.